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Boron-doped α-$Ni(OH)_2$ nanoflowers with high specific surface area as electrochemical capacitor materials

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ABSTRACT

The boron-doped α-$Ni(OH)_2$ nanoflowers (B-α-$Ni(OH)_2$) with high specific surface area (400 $m^2\ g^{-1}$) were synthesized by the one pot liquid-phase method using P123 ($EO_{20}PO_{70}EO_{20}$) as template and $NaBH_4$ as alkali and boron sources. The size of the B-α-$Ni(OH)_2$ nanoflowers is about 300 nm and there are many porous. The 50 nm nanoplates are the basic structure units of nanoflowers and thickness of the nanosheets is approximately 5 nm. The content of B is about 15% among the Ni, B, O elements and boron exists mainly in the form of BO_2^-, which was confirmed by XPS characterization. B-α-$Ni(OH)_2$ nanoflowers exhibit a high specific capacitance of ~2296 $F\ g^{-1}$ at a charge and discharge current density of 3 $A\ g^{-1}$ with excellent cycling ability. The high specific capacitance and remarkable rate capability are promising for applications of B-α-$Ni(OH)_2$ nanostructures as advanced electrochemical capacitor materials with both high energy and cycling ability.

1. Introduction

The increasing growing concerns about air pollution and demand for energy have stimulated intense research on energy storage and conversion from renewable clean energy [1,2]. Electrochemical supercapacitors (ES), the promising power sources for automotive applications and portable systems are considered as a promising candidate for energy storage [3]. There are two types of ES, pseudocapacitor and electrochemical double-layer capacitor (EDLC) [4]. As to EDLC, charge exists at the interface between electrode and electrolyte. As to pseudocapacitor, there are always faradic redox reactions between an electrolyte and active material such as a metal hydroxides, metal oxide and conducting polymer [5]. Pseudocapacitor has a higher specific capacitance than EDLC. Nickel hydroxide has been recognized as a promising electrode material in electrochemical capacitors due to its well defined redox activity, diversity synthesis methods and inexpensive raw materials [6,7].

α-$Ni(OH)_2$ and β-$Ni(OH)_2$ phases are the two polymorphs of $Ni(OH)_2$ which have a hexagonal-layered structure [8]. Because α-$Ni(OH)_2$ gives higher capacity than β-$Ni(OH)_2$ [9], it has a high potential as an electrode material. However, α-$Ni(OH)_2$ is unstable and quickly converts into β-$Ni(OH)_2$ phase under alkaline media leading to the reduced capacity and poor circulation [10,11]. So prevention of ageing of α-$Ni(OH)_2$ and therefore improving cycling ability are a primary concern and challenge [12]. Furthermore, because of the high specific surface area, fast redox reactions, and shortened diffusion path in solid phase, nanostructured materials become more and more important in the capacitors field [13]. Increasing the surface area by synthesis of porous nanostructured $Ni(OH)_2$ materials to improve the specific capacitance is another efficient method.

In the present work, we have synthesized the boron-doped α-$Ni(OH)_2$ nanoflowers (B-α-$Ni(OH)_2$), which exhibit high specific capacitance and stability.

2. Experimental

Reagents: Nafion (5 wt% ethanol solution) was purchased from Alfa Aesar, and diluted to 0.1 wt% with doubly distilled water. The surfactant copolymer poly (ethylene oxide)–poly (propylene

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oxide)–poly (ethylene oxide), is commercially known as Pluronic (P123 EO_{20}–PO_{70}–EO_{20}). Sodium borohydride was obtained from Sinopharm Chemical Reagent Co., Ltd. Polytetrafluoroethylene (PTFE, 60 wt% water suspension) was from Aladdin. Other chemicals were all analytical reagents from Beijing Chemical Company. All stock solutions were prepared with deionized water resistively not less than 18.2 MΩ cm.

Synthesis of materials: The synthesis of B-α-$Ni(OH)_2$ was based on a self-assembly between a triblock copolymer template P_{123} and two precursors (sodium borohydride and nickel species) in a flask. 40 ml solution of $Ni(NO_3)_2$ $6H_2O$ (8.6 g) was put into the 400 ml solution of P123 (4 g), and then stirring at 313 K for 2 h. When the temperature drops to ambient temperature, the 20 ml sodium borohydride (1.5 g) solution was dropped into the mixture. After 2 h, the same quantity of sodium borohydride solution was added into the mixture, too. After 200 min, light green sediments were formed. The mixture was filtered and washed many times with water and ethanol alternately until no foam of surfactant P_{123} in the filtrate, then we got B-α-$Ni(OH)_2$. We could obtain the α-$Ni(OH)_2$ by replacing sodium borohydride with sodium hydroxide. The Twice-B-α-$Ni(OH)_2$ was synthesized by adding twice the amount of sodium borohydride.

Preparation nickel electrodes and electrochemical measurements: A three-electrode system was used. Ag/AgCl electrode was used as reference electrode, 1 M aqueous solution of KOH was used as electrolyte. The working electrode was prepared as follows: B-α-$Ni(OH)_2$ was first mixed with polytetrafluoroethylene (PTFE) and acetylene black at a given weight ratio (90:5:5). The mixture was dispersed in ethanol, the suspension was drop-dried into a 1 cm × 1 cm Ni foam. Then the foam dried at 333 K for 12 h, then pressed it at 10 MPa. Before testing, the compact foam was immersed in the electrolyte for 24 h.

The steady-state cyclic voltammograms (CVs) were recorded on a CHI660D electrochemical workstation (CHI, Shanghai) at 298 K. The below formula was employed as equation for calculation average specific capacitance values from the CV curves.

$$C = \frac{\int I\,dt}{m\Delta V} \tag{1}$$

where I means the oxidation or reduction current, m indicates the mass of the active electrode material, dt indicates time differential, and ΔV is the voltage range of one sweep segment. And there is another method as the following formula:

$$C = \frac{I\Delta t}{m\Delta V} \tag{2}$$

While, where I represents charge or discharge current, Δt indicates the time for a full charge or discharge, ΔV is the voltage change after a full charge or discharge and m is the mass of the active material.

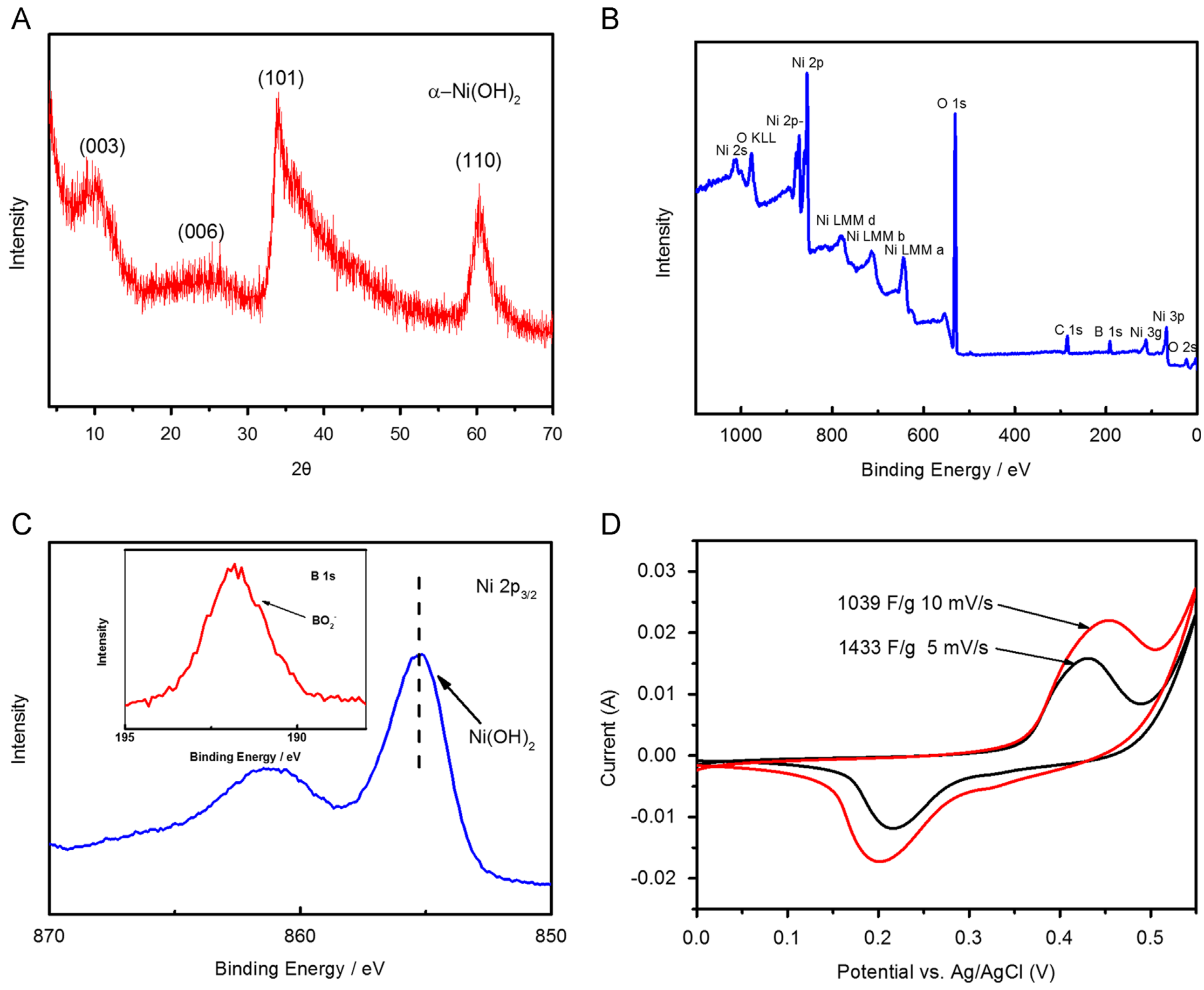

Fig. 1. XRD pattern (A), XPS spectroscopy (B), XPS Ni 2p (inset: XPS B 1s) (C) and CV curves (D) of B-α-$Ni(OH)_2$.